Synchrotron X-ray Diffraction and the Solid State Chemistry Community

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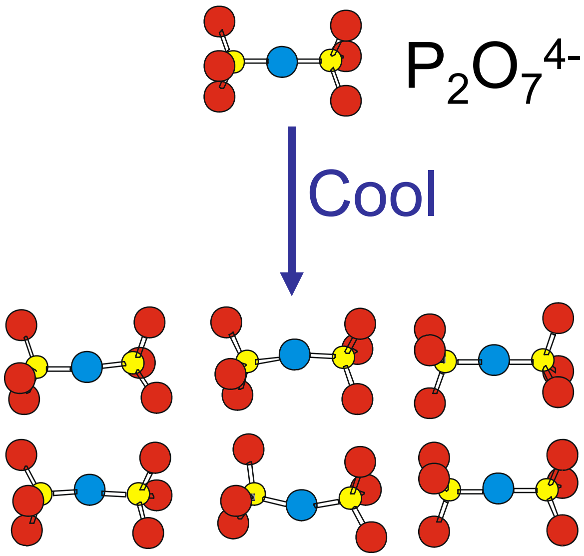
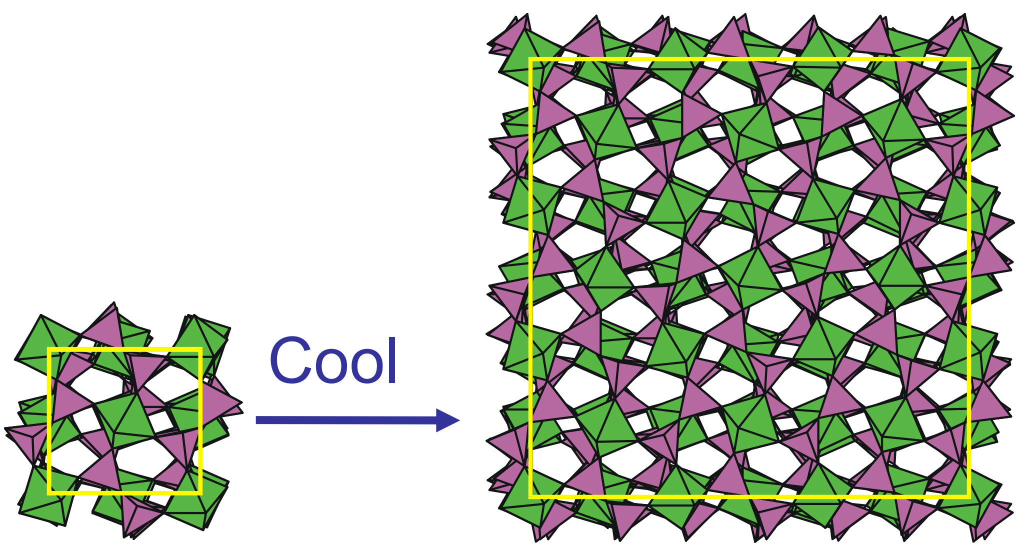
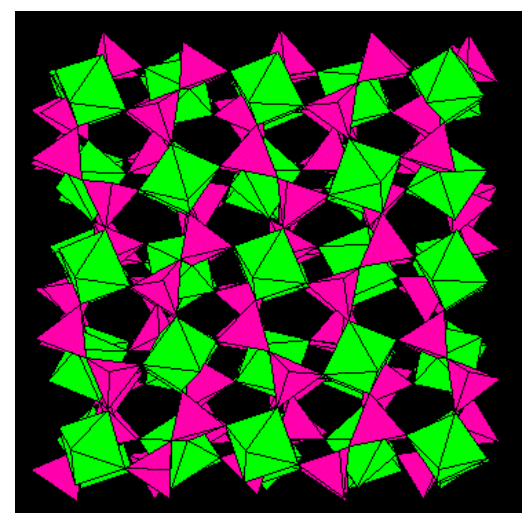
ZrP_2O_7 Structural Frustration



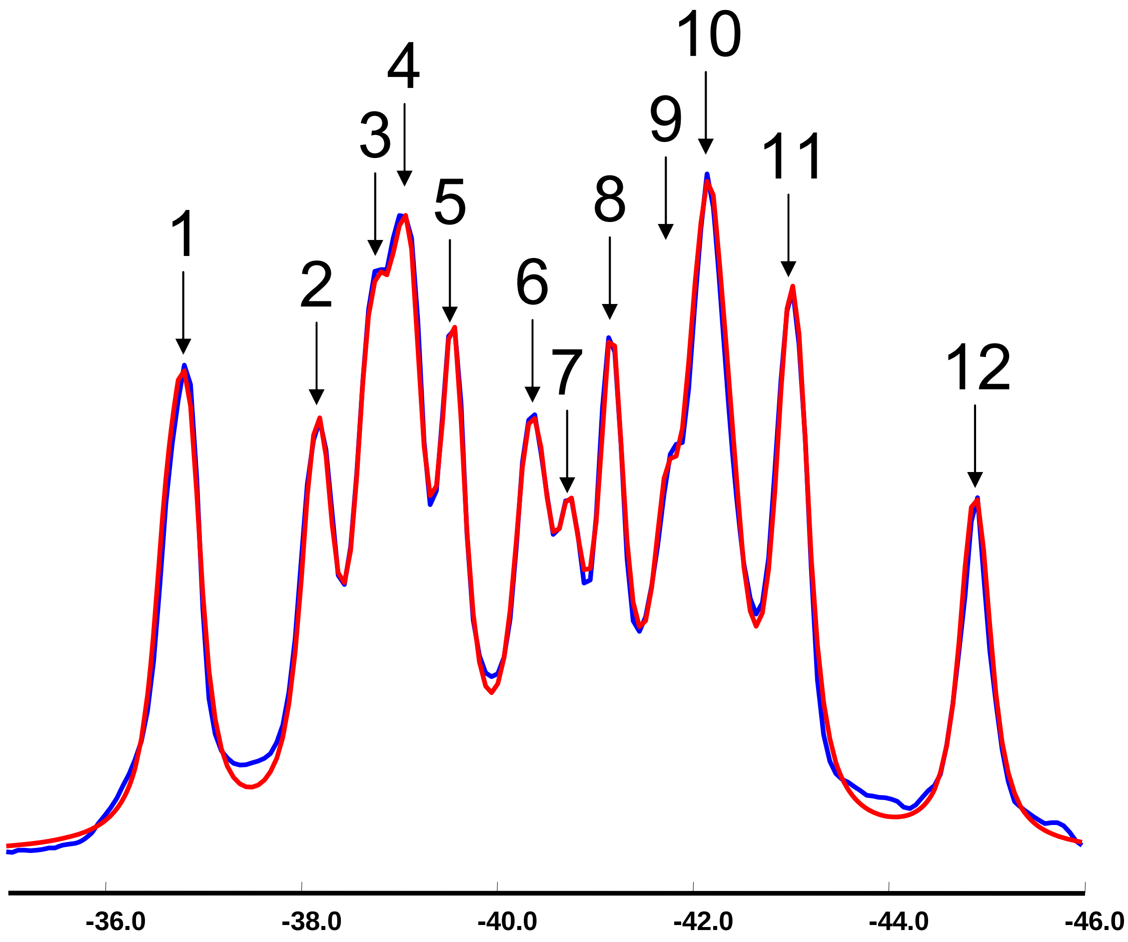
- P-O-P bonds bend
- Symmetry of material is reduced
- Supercell formed
- Pa-3 1x1x1 to Pa-3 3x3x3
- 50 atoms in asymmetric unit
- 11 unique P sites





Courtesy of John Evans at Durham University

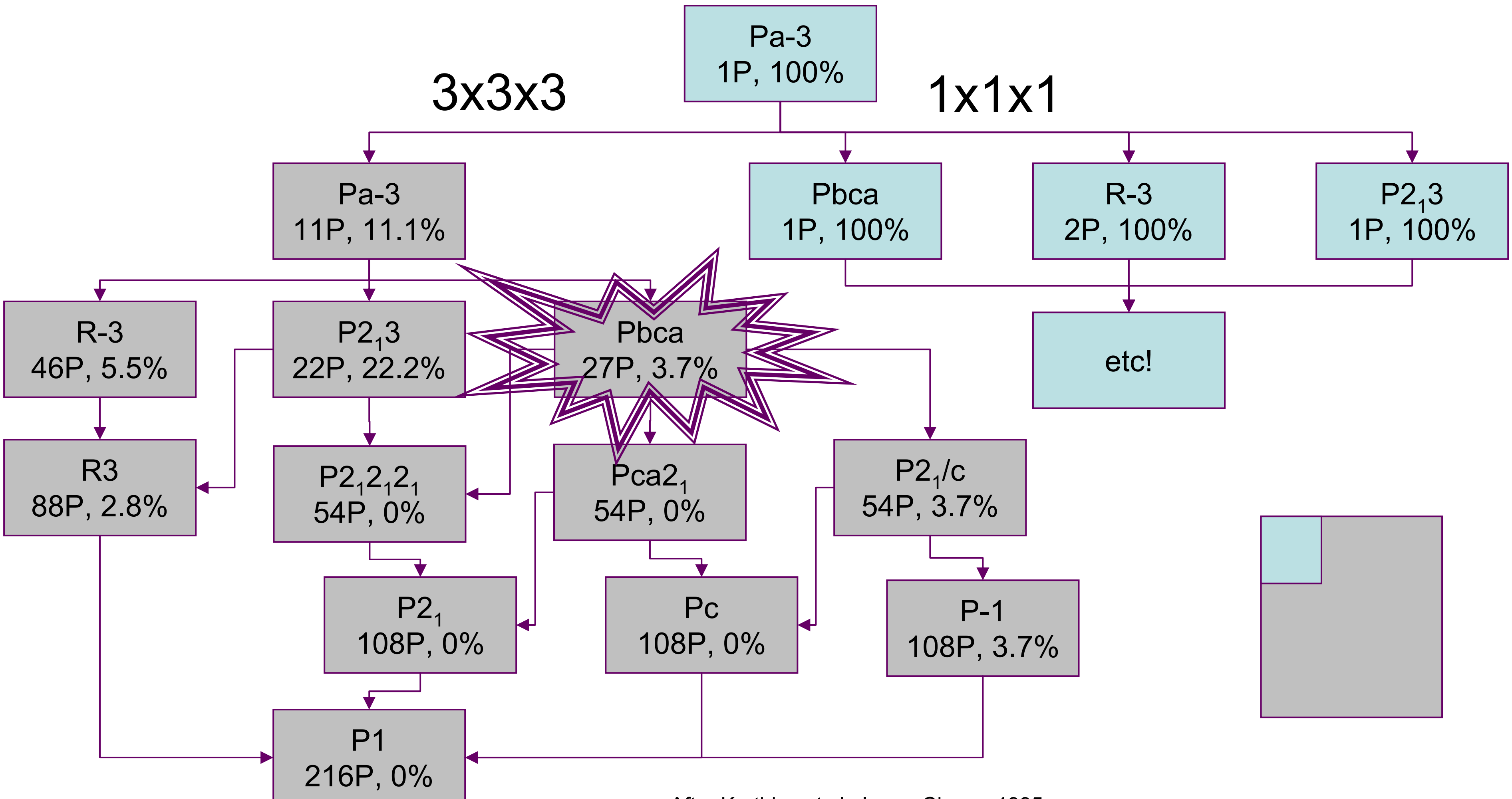
ZrP_2O_7 1D ^{31}P Solid State NMR



- 1D ^{31}P NMR MAS 10 MHz
- Shows a number of unique phosphorus sites
- At least 12 sites visible
- Expect only 11
- Ian King, Franck Fayon

Courtesy of John Evans at Durham University

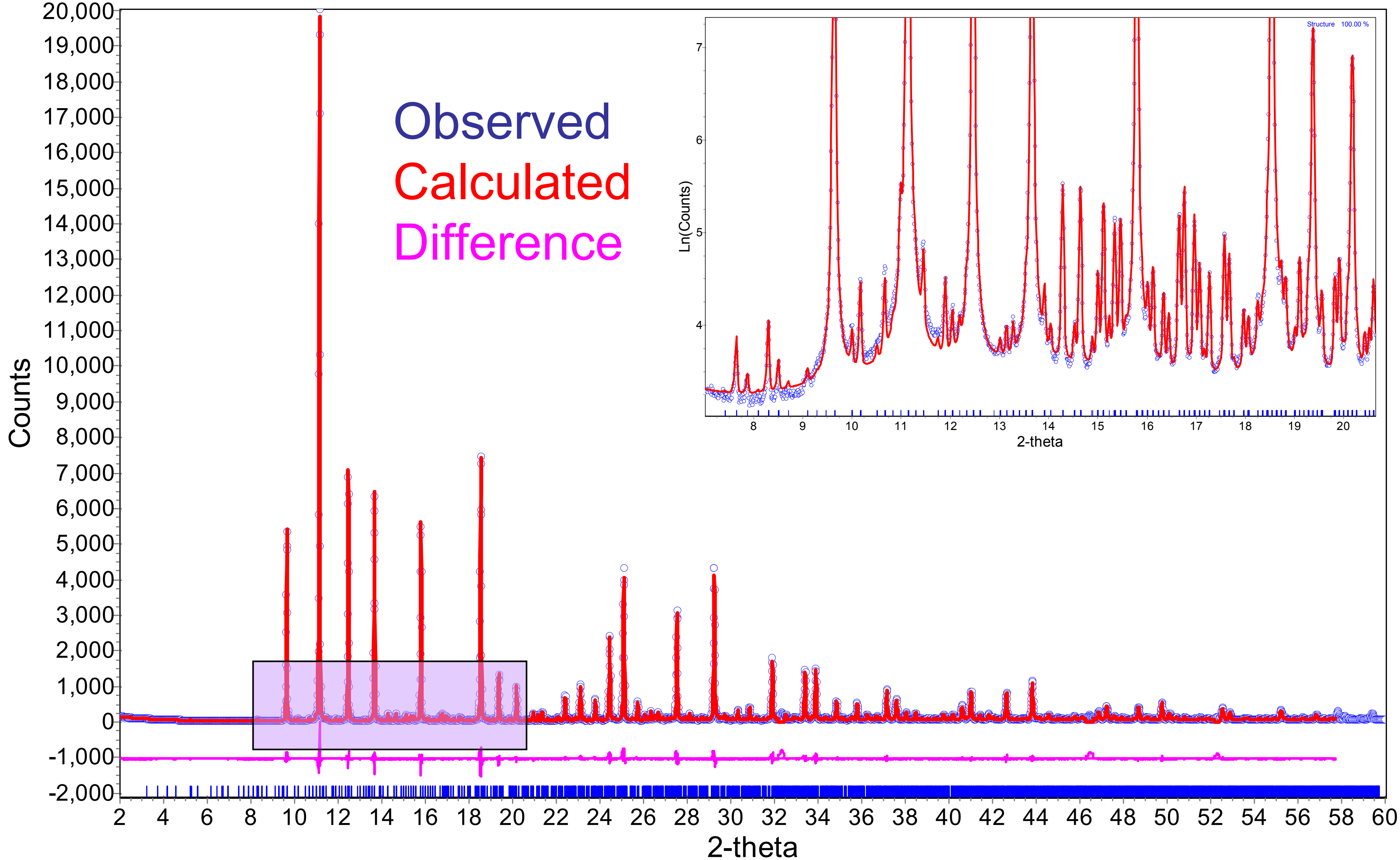
ZrP_2O_7 Phase Transitions



After Korthius et al., Inorg. Chem., 1995

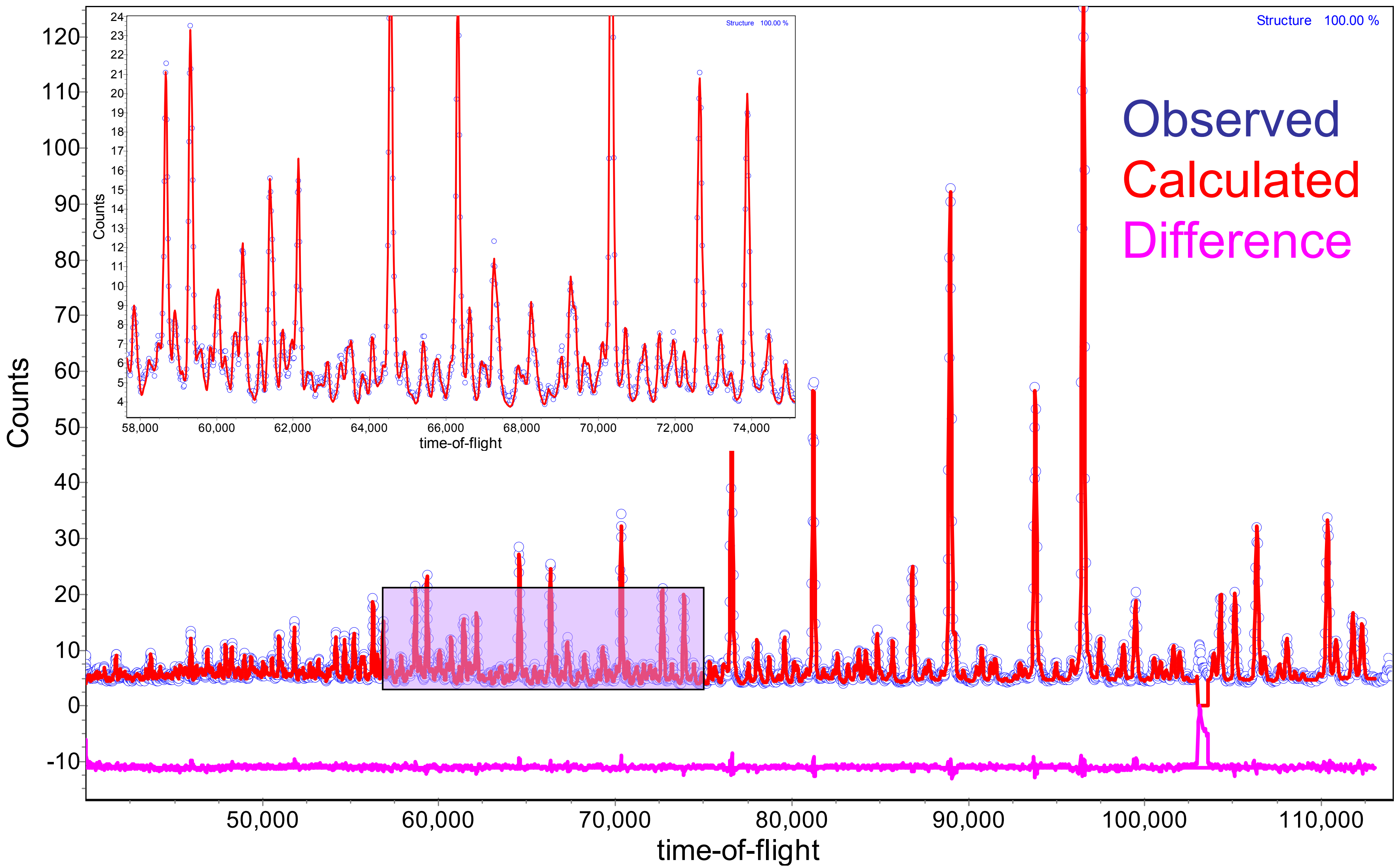
Courtesy of John Evans at Durham University

ZrP_2O_7 X ray Rietveld Plot



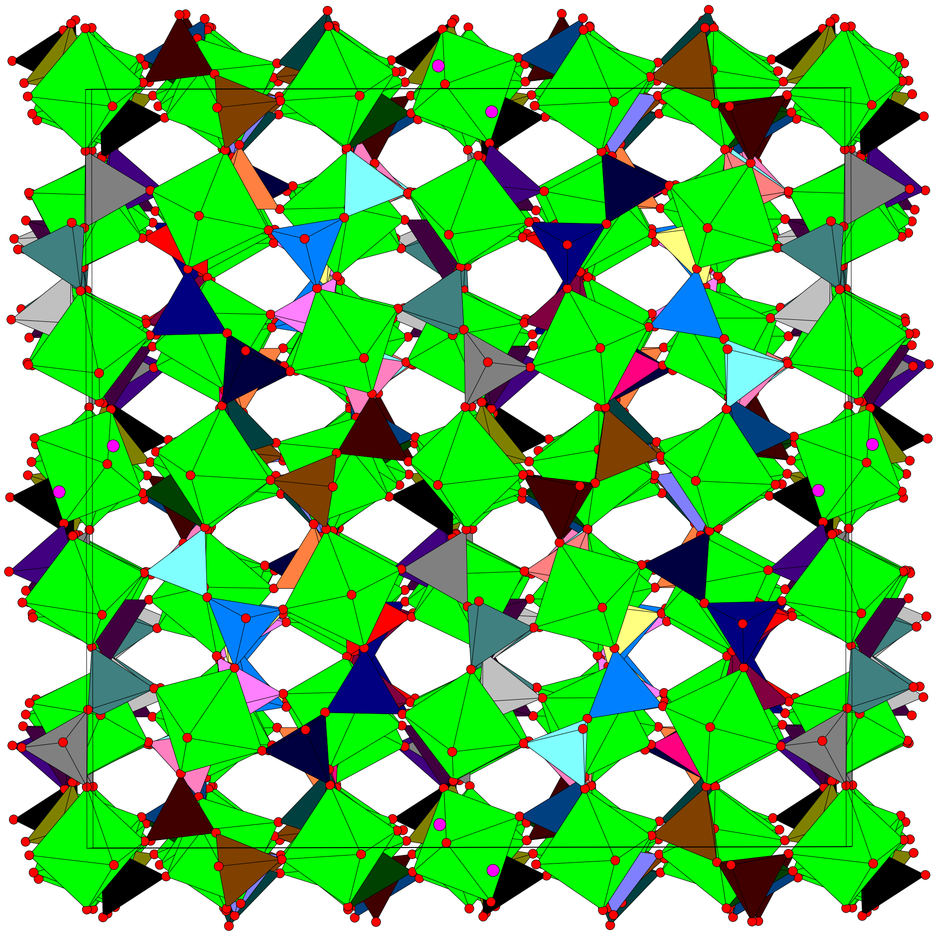
Courtesy of John Evans at Durham University

ZrP_2O_7 Neutron Rietveld Plot



Courtesy of John Evans at Durham University

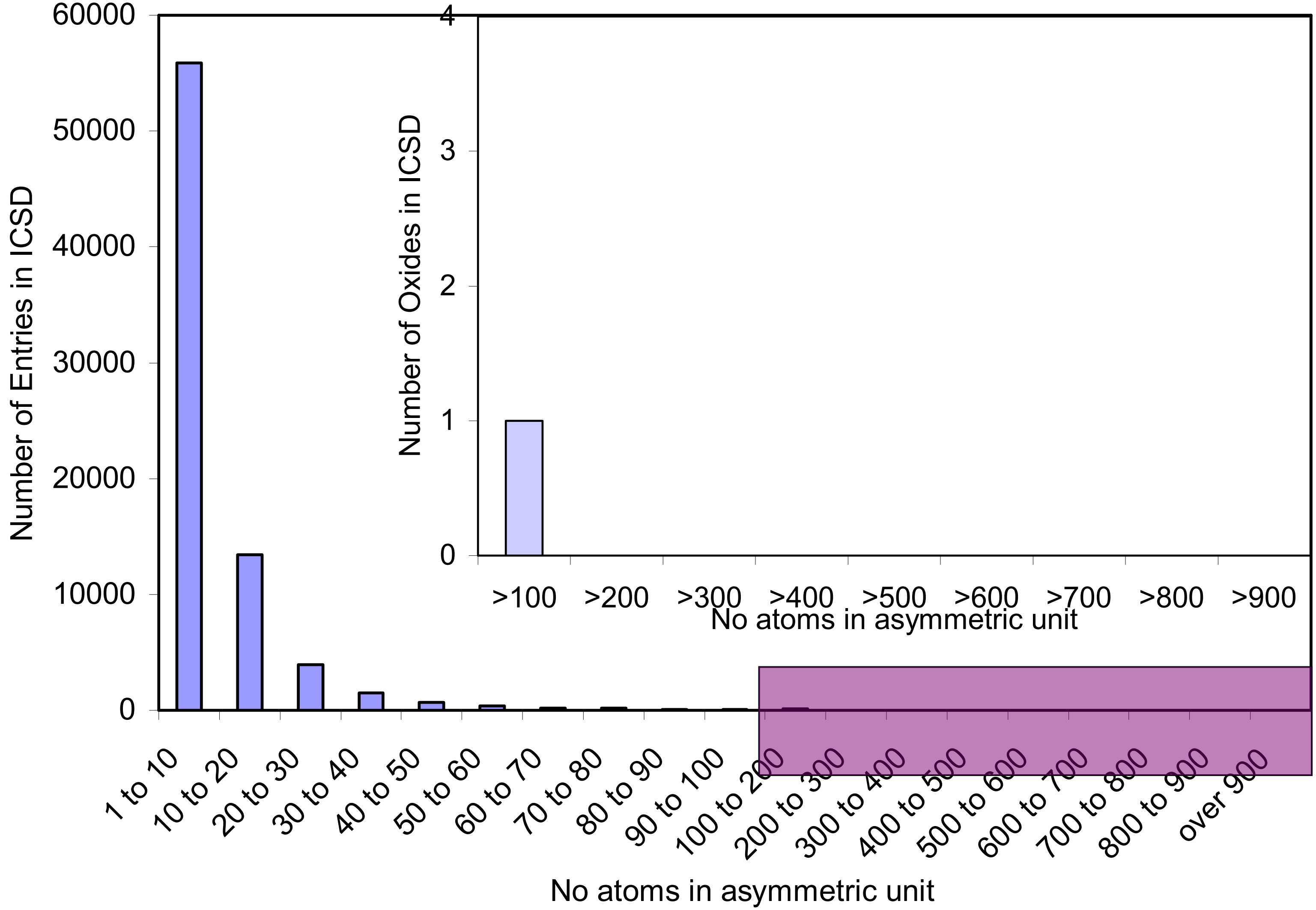
ZrP_2O_7 Structure



- Pbca
- a = 24.7437 Å
- b = 24.7258 Å
- c = 24.7507 Å
- 136 atoms in asymmetric unit
- 27 P
- 14 Zr
- Errors < 0.06 Å

Courtesy of John Evans at Durham University

Structural Complexity: Oxides



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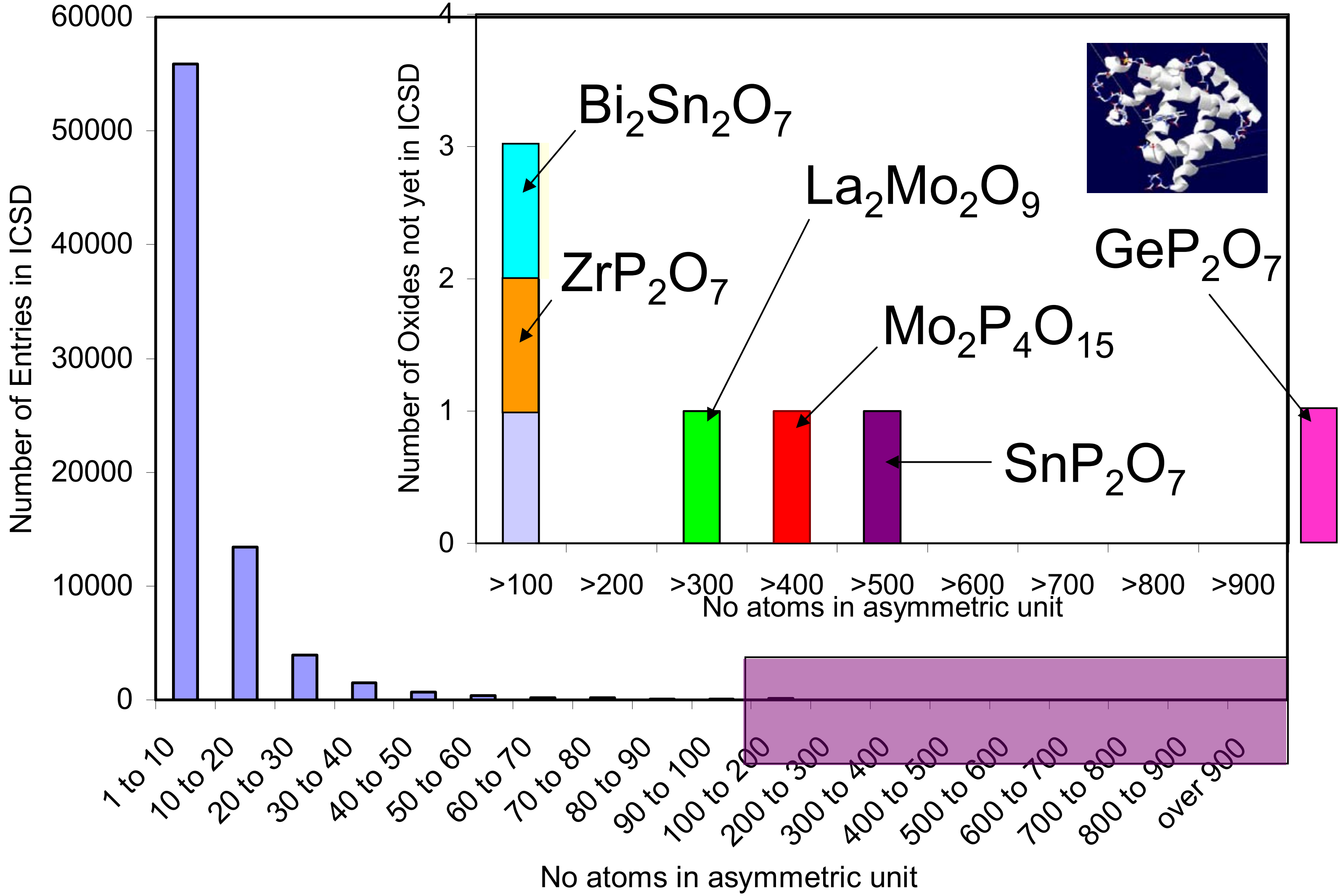
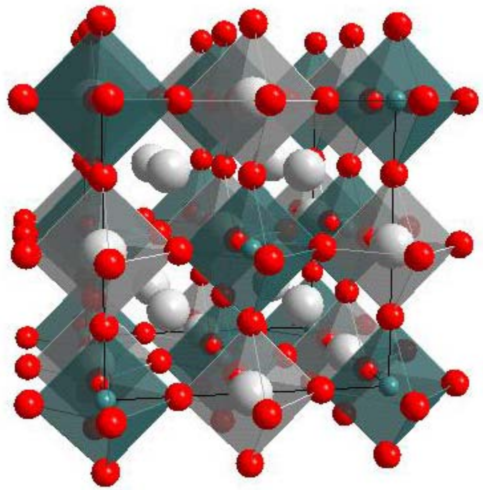
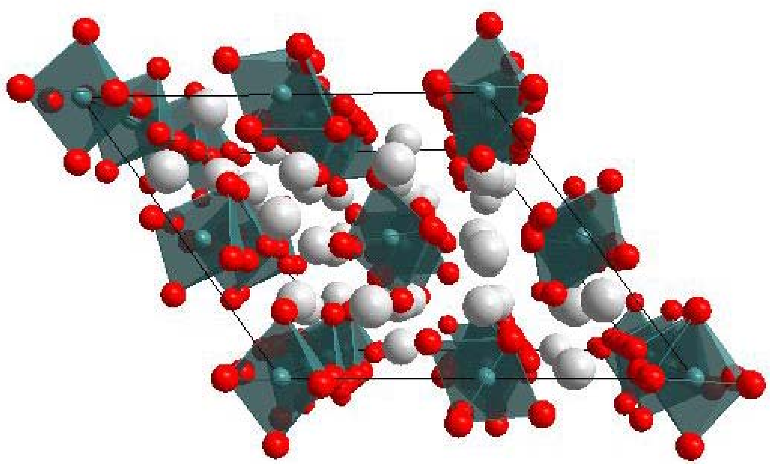


Sr_3WO_6
Complex Octahedral Tilting in a Cryolite Structure



T > 1320 K
Space group: Fm3m (Cubic)
Unit Cell:
  $a \cong 8.5$ Å
Asymmetric Unit: 4 Atoms

Broken Connectivity Tilting



470 K < T < 1320 K
Space group: A2/m (Monoclinic)
Unit Cell:
  a = 11.86 Å, b = 17.72 Å, c = 10.13 Å,
  α = 90°, β = 125.5°, γ = 90°
Asymmetric Unit: 20 Atoms

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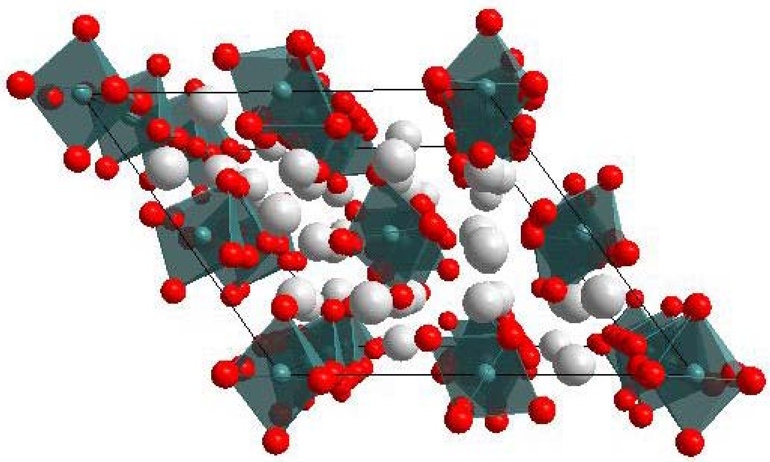


Broken Connectivity Tilting

T > 470 K

Space group: P-1 (Triclinic)

Unit Cell:

a = 11.82 Å, b = 17.65 Å, c = 10.16 Å,

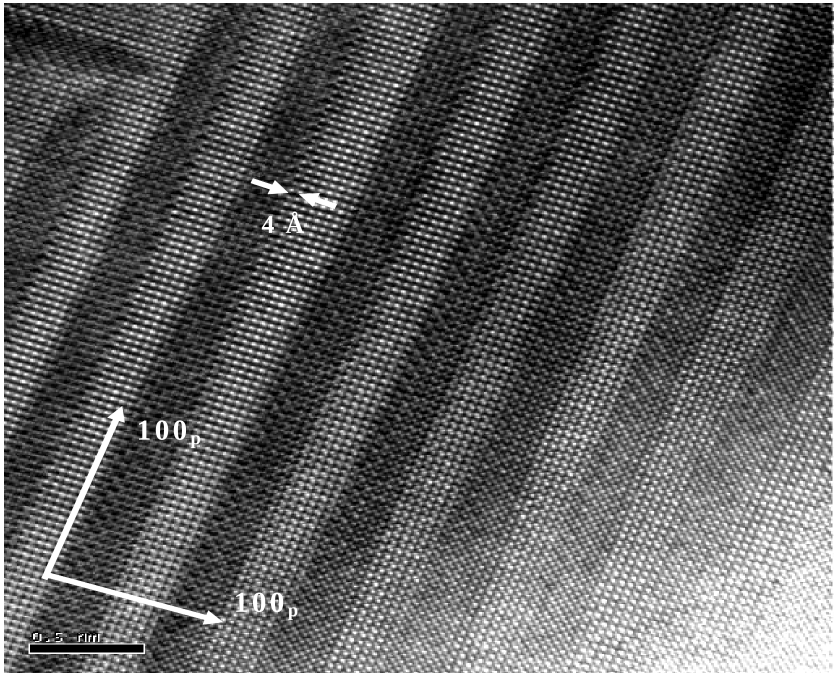
α= 89.79° β = 125.95° γ = 90.41°

Asymmetric Unit: 64 Atoms

?

$NaLaMgWO_6$ Electron Microscopy

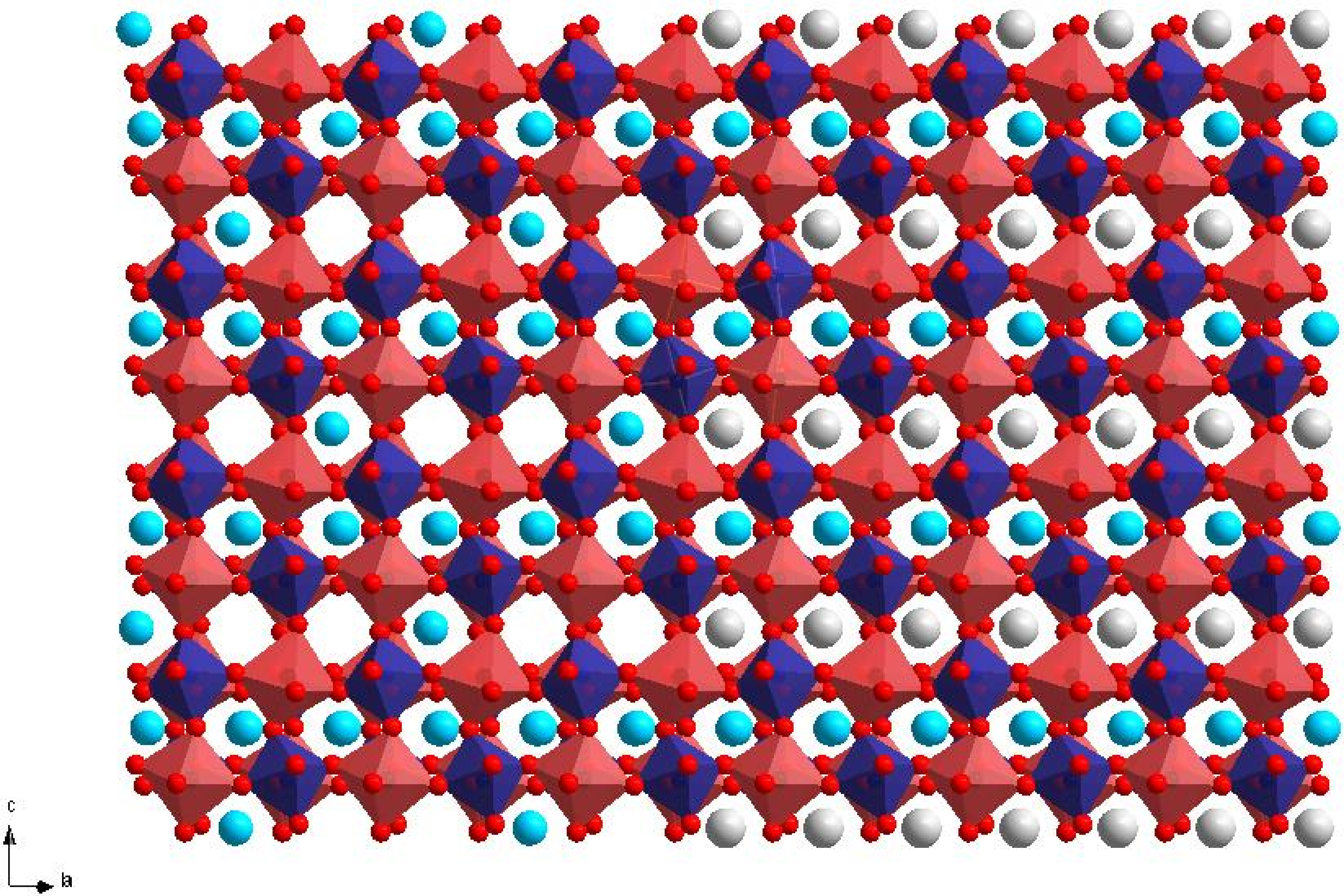
Electron Diffraction Pattern



HRTEM Image

Suggests a $12a_p$ unit cell repeat in the *a*-direction (perpendicular to the Na/La ordering)

Proposed Model – Periodic Phase Separation in $Na_{1-x}La_{1+x/3}MgWO_6$



Comments from Solid State Community

- **Hanno zur Loye (University of South Carolina)**
  - *It would be nicest if we could simply send a capillary containing our powder and have someone run it and send us the data back. Variable temperature capabilities, to look for phase transitions would be great (though I realize this cannot be done via mail in). Having some decent computers there for data collection, data conversion and analysis would be helpful. Maybe we can graduate from VMS.*
- **Svilen Bobev (University of Delaware)**
  - *Advanced capabilities at NSLS to do high resolution powder and single-crystal diffraction. Special environments for low/high T and under magnetic field will be fantastic.*
- **Mike Lufaso (University of North Florida)**
  - *One aspect that I would find particularly useful is the implementation of a 'mail-order program' for routine powder diffraction measurements.*

Comments from Solid State Community

- **Ram Seshadri (UCSB)**
  - *Temperature control, particularly below 10 K is what all diffractometers miss that we need.*
- **Cora Lind (University of Toledo)**
  - *A setup with a highly focused beam (for the small opening of the DAC), ability to choose a short wavelength (to get data with a 22 degree cone opening), and most importantly a good detector (we have to run a gazillion data corrections every time before we can do anything useful) are highly desirable.*

Comments from Solid State Community

- **Ken Poeppelmeier (Northwestern University)**
  - *a purposeful, "user interface" is needed from providing stipend resources, travel funds, to an effective software, web-friendly interface (much as we do with the journals)....this MUST be built in from the get-go...not left as a promise that gets underfunded or not funded at all down the road. There simply are no funds in the grants of the PI to do this !!!*
- **Ray Schaak (Penn State University)**
  - *One of my main interests in this area would be analyzing structures of nanoscale solids, most likely PDF-type analysis. We've not done it yet, but that is a very definite emerging need. We and others sometimes observe the formation of phases, as nanocrystals made at low-ish temperatures, that are "new" or typically only observed under higher temperature or pressure conditions. Probing these structures… will be critical.*

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Take Home Messages

- Many of the challenging problems in solid state chemistry involve superstructures. Keys to solving these problems include:
  - High resolution
  - Low background/excellent signal-to-noise
  - Variable temperature studies are important
- Links with other techniques are critical
  - Neutron diffraction
  - Electron diffraction
  - Solid state NMR
  - Symmetry analysis
- Solid State Chemists Needs
  - Rapid access/mail in for most work
  - Variable temperature/pressure capabilities
  - PDF studies are likely to grow in importance